Polyoxometalate-based 3D porous framework with inorganic molecular nanocage units

SHAOBIN LI*, ZIHAO LI, JINGYU ZHANG, ZHENGNAN SU, SHIYING QI, SHIHONG GUO and XIAOGUO TAN

College of Materials Science and Engineering, Qiqihar University, Qiqihar 161006, China
Email: qqhrlsb1022@126.com

MS received 25 November 2016; revised 9 February 2017; accepted 22 March 2017

Abstract. A new polyoxometalate-based 3D porous framework with inorganic molecular nanocage unit, \((\text{H}_2\text{dap})[\text{K(H}_2\text{O)}_2(V_{10}\text{O}_{28})_{0.5}]\) (1) (dap = 1,2-diaminopropane), has been synthesized and characterized by routine methods. In 1, the decavanadate clusters, as twelve-dentate connectors, link eight potassium ions to form a 3D porous framework with inorganic molecular cage units. There are two dap ligand molecules occupying in each inorganic molecular cage. Furthermore, the electrochemical properties of 1 were studied, which indicate that 1 has a good electrocatalytic activity towards reduction of iodate \((\text{IO}_3^-)\) ascribed to the V-center.

Keywords. Polyoxometalates; inorganic nanocage; 3d porous framework; electrochemistry; electrocatalysis.

1. Introduction

Molecular cage is of great interest not only because of their well-defined cavities and structural characteristics that can incorporate various guest species for chemical reactivity, but also for their potential applications in catalysis, gas separation and storage.1–7 During the past few decades, self-assembly of molecular cages with various sizes and shapes has been extensively explored. Polyoxometalates (POMs), as a large family of metal-oxygen clusters, have been extensively studied due not only to their unmatched structural types and attractive properties such as a controllable shape, size, high negative charge, and nucleophilic oxygen-enriched surface, but also for various potential applications in catalysis, medicine and materials science.8–17 The design and synthesis of POM-based molecular cages might merge POM’s merits to generate extra-large nanosized cages with special properties. Thus, the POM-based molecular cages have gained the attention of chemists. To date, thanks to the work of POM chemists, some novel POM-based molecular cages have been successfully synthesized. It is notable that Lu et al., successfully made a discrete adamantane-like cage in 2010;18 in the same year, Yang et al., reported a discrete POM-based organic cage based Ni₁₆-substituted POMs19 and Wang et al., reported a 3D porous framework with two types of cubic cages.20 Recently, Su et al., obtained a cage structure based on P₃Zn₁₆ cluster,21 and Niu et al., isolated a inorganic-organic molecular cage based on AsMo₆ cluster.22 Inspired by these pioneering work, in our present work, we report POM-based molecular cages.

Herein, we report the preparation and structure of a new polyoxometalate-based 3D porous framework with inorganic molecular cage units, \((\text{H}_2\text{dap})[\text{K(H}_2\text{O)}_2(V_{10}\text{O}_{28})_{0.5}]\) (1) (dap = 1,2-diaminopropane), which exhibits a \((4,8)\)-connected 3D framework with a novel \((4^6)(4^{11} \cdot 6^{13}) \cdot 8^2\) topology. To the best of our knowledge, to date, it represents the first decavanadate-based 3D porous framework with inorganic molecular cage unit.

2. Experimental

2.1 Materials and methods

All chemicals were of reagent grade and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 2400 CHN Elemental Analyzer. The FT-IR spectra were recorded in KBr pellets in the range 4000–400 cm⁻¹ with a Nicolet AVATAR FT-IR360 spectrometer. X-ray photoelectron spectrum (XPS) was recorded on an ESCALAB-MKII spectrometer. A CHI660 electrochemical workstation was used for controlled electrochemical measurements and data collection. A conventional three-electrode system was used, with carbon paste electrode (CPE) as working electrode, commercial Ag/AgCl as reference electrode and twisted platinum wire as counter electrode.
2.2 Synthesis of compound 1

NaVO₃ (0.26 g, 2.13 mmol) and H₃BO₃ (0.16 g, 2.58 mmol) were dissolved in water (15 mL), and stirred for 1 h at 80°C. KCl (0.36 g, 4.83 mmol) and 1,2-diaminopropane (dap) (0.3 mL) were added to the above solution at 80°C. Stirred for 2 h with a starting pH = 4.85, adjusted by 1 M CH₃COOH. Then, the solution was cooled to room temperature and filtered. Slow evaporation at room temperature resulted in yellow crystals of 1 after 10 days with a yield 51% based on V. Anal. calcd. for 1: H, 2.40; C, 5.73; N, 4.45; K, 6.22; V, 40.50 (%). Found: H, 2.31; C, 5.84; N, 4.34; K, 6.34; V, 40.84 (%).

2.3 X-ray crystallographic study

A single crystal of 1 was carefully selected for single-crystal X-ray diffraction analysis. Data collection was performed on a Rigaku RAXIS-RAPID equipped with a narrow-focus, 5.4 kW sealed tube X-ray source (graphite-monochromated MoKα radiation, λ = 0.71073 Å). The data was collected at 293 K. The data processing was accomplished with the PROCESS-AUTO processing program. The structure of 1 was solved by direct methods and refined by full-matrix least-squares on $F^2$ using the SHELXTL 97 crystallographic software package. Anisotropic displacement parameters were used to refine all non-hydrogen atoms. The organic hydrogen atoms were generated geometrically. The hydrogen atoms of the water molecule in 1 could not be introduced but were included in the structure factor calculation. Details of the X-ray structure analysis are given in Table 1. Selected bond lengths and angles are listed in Table S1 (in Supplementary Information). Crystal data and structure refinement, bond lengths and angles, and anisotropic displacement parameters are available in supplementary crystallographic data.

3. Results and Discussion

It is worth noting that the use of boric acid was necessary in the synthesis of compound 1, although it is not present in the final structure; we could not obtain compound 1 without it.

<table>
<thead>
<tr>
<th>Table 1. Crystal data and structure refinement for 1.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Empirical formula</strong></td>
</tr>
<tr>
<td>Formula weight</td>
</tr>
<tr>
<td>Color</td>
</tr>
<tr>
<td>Crystal size, mm³</td>
</tr>
<tr>
<td>Crystal system</td>
</tr>
<tr>
<td>Space group</td>
</tr>
<tr>
<td>a Å</td>
</tr>
<tr>
<td>b Å</td>
</tr>
<tr>
<td>c Å</td>
</tr>
<tr>
<td>α, deg</td>
</tr>
<tr>
<td>β, deg</td>
</tr>
<tr>
<td>γ, deg</td>
</tr>
<tr>
<td>Volume, Å³</td>
</tr>
<tr>
<td>Z</td>
</tr>
<tr>
<td>Dc, g cm⁻³</td>
</tr>
<tr>
<td>$\mu$ (MoKα), mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
</tr>
<tr>
<td>hkl Range</td>
</tr>
<tr>
<td>Refl. measured/unique</td>
</tr>
<tr>
<td>Rint</td>
</tr>
<tr>
<td>Data/parameters</td>
</tr>
<tr>
<td>GOF on F²</td>
</tr>
<tr>
<td>$R_1$, wR² [ I &gt; 2σ(I)]¹,²</td>
</tr>
<tr>
<td>$R_1$, wR² (all data)</td>
</tr>
<tr>
<td>$\Delta$$\rho_{\text{min}}$ (max/min), e Å⁻³</td>
</tr>
<tr>
<td>Highest peak</td>
</tr>
<tr>
<td>Deepest hole</td>
</tr>
</tbody>
</table>

¹ $R_1 = \Sigma||F_o| − |F_c||/\Sigma|F_o|;$ ² $wR² = \left(\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2\right)^{1/2}$. 
3.1 Description of crystal structure

The single-crystal X-ray diffraction analysis has revealed that I consists of one V$_{10}$O$_{28}^4-$ anion (abbreviated as V$_{10}$), one K$^+$ cation, one biprotonated dap ligand and two coordinated water molecules, as shown in Figure 1. The V atoms are in +5 oxidation state confirmed by BVS calculations$^{24}$ (Table S2) and XPS spectrum (Figure S1, in Supplementary Information).

There is one crystallographically independent K ion in I, which interacts with eight O atoms, two from water molecules and six from four V$_{10}$ anions (Figure 2a). The bond lengths and angles around the K ion are in the ranges of 2.763(2)–3.034(2) Å (K–O) and 54.11(6)–163.58(4)$^\circ$ (O–K–O). All of these bond lengths and angles are within the normal ranges observed in other K-containing complexes.$^{25}$ The centrosymmetric polyanion consists of five independent [VO$_6$]$_2^-$ sharing edges, and has approximate $D_{2h}$ symmetry. The bond lengths and angles of the decavanadate anion show a similar trend to those reported in the literature.$^{26,27}$ The asymmetric unit in the crystal structure of I consists of one crystallographically independent monovalent lacunary Lindqvist anion. Two monovalent lacunary Lindqvist anions are linked through sharing of two [VO$_6$]$_2^-$ that make up of the decavanadate anion. As shown in Figure 2b, each V$_{10}$ cluster acts as a twelve-dentate inorganic ligand, covalently bonded to eight K ions (K1, K1#1, K1#2, K1#3, K1#4, K1#5, K1#6 and K1#7).

One of the structural features of I is that each V$_{10}$ cluster, as twelve-dentate inorganic ligand, links eight potassium ions to form a 3D porous framework. From the topological view, each K1 cation is considered as a 4-connected node and V$_{10}$ cluster is considered as 8-connected node. The structure of I can be simplified as a novel 3D (4,8)-connected framework with a (4$^5$)(4$^{11}$ · 61$^1$ · 8$^4$) topology (Figure 3). The more aesthetically pleasing structural feature is the inorganic molecular cage with an inner cavity diameter of approximately 5.68 Å, which is constructed by six K cations linking six V$_{10}$ clusters (Figure 2d). Interestingly, there are two free dap ligands in each inorganic molecular cage. To the best of our knowledge, it represents the first example of V$_{10}$-based 3D porous framework with inorganic molecular cage units, to date.

3.2 IR spectrum

The IR spectrum of compound I (Figure S2 in SI) exhibits the characteristic peaks at 953, 832 and 745 cm$^{-1}$, which are attributed to $\nu$(V – O$_b$) and $\nu_{as}$(V – O$_b$ – V), respectively. Compared to the typical decavanadate cluster, compound I has similar peaks in the range of 730–960 cm$^{-1}$ except for slight shifts of peaks due to the interactions between the V$_{10}$ anions and the K$^+$ in the solid state, which indicates that the V$_{10}$ cluster in the title compound still retains the basic structure of decavanadate anion.$^{28}$ The bands in the region of 1631–1113 cm$^{-1}$ could be ascribed to the characteristic peaks of dap ligand. Additionally, the broad band at 3461 cm$^{-1}$ is associated with the water molecule.

3.3 Electrochemical properties

In order to study the redox properties of title compound, the cyclic voltammetric behavior of I was measured in 0.5 M H$_2$SO$_4$–Na$_2$SO$_4$ solution (pH = 2.75, 10 mL). In the potential range from +0.40 to −0.1 V, there are two pairs of redox peaks (I–I′, II–II′), and the average peak potentials, $E_{1/2} = (E_{pa} + E_{pc})/2$, are ca. 0.16 and 0.08 V, which are ascribed to one-electron vanadium-centered V$^{V} \rightarrow$ V$^{IV}$ redox process.$^{29,30}$ As shown in the inset of Figure 4, when the scan rates are varied from 0.1 to 0.6 V s$^{-1}$, the peak potentials change gradually: the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials to the positive direction with increasing scan rates. The peak currents are proportional to the scan rate, which indicates that the redox processes are surface-controlled.$^{31}$

The POMs have been exploited extensively in electrocatalytic reactions and in applications such as biosensors and fuel cells.$^{32,33}$ Here, the reduction of IO$_3^-$ was chosen as a test reaction to study the electrocatalytic activity of I. As shown in Figure 5, it
Figure 2. (a, b) The coordination relation between the K cation and V10 cluster; (c) the 3D porous framework; and (d) the inorganic molecular cage.

Figure 3. The topology structure of 3D porous framework in 1.

Figure 4. Cyclic voltammograms for 1 in 0.5 M H2SO4—Na2SO4 solution at different scan rates (from inner to outer): 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 V s−1.

Figure 5. Cyclic voltammograms for 1 in 0.5 M H2SO4—Na2SO4 solution (pH = 2.75) containing 70 mM iodate.

Figure 6. Cyclic voltammograms for 1 in 0.5 M H2SO4—Na2SO4 solution (pH = 2.75) containing 70 mM iodate.

displayed good electrocatalytic activity towards the reduction of IO3− in 0.5 M H2SO4—Na2SO4 solution (pH = 2.75). With the addition of IO3−, the cathodic peak II substantially increased, while the corresponding anodic peak current decreased. The inset of Figure 5 shows the relationship between the cathodic peak currents of the second wave and concentration of IO3−. The electrocatalytic efficiency of 1 (based on a rough calculation using CAT formula) toward the reduction of IO3− was ca. 190% at 0.5 M H2SO4—Na2SO4 solution (pH = 2.75) containing 70 mM iodate.

Additionally, the stability of 1 was investigated by scanning for 50 cycles in 0.5 M H2SO4—Na2SO4 solution (pH = 2.75). As shown in Figure 6, it can be seen that the electrode exhibits almost no loss in the current signal after 50 cycles, which suggests that catalyst 1 has high stability.
Polyoxometalate-based inorganic nanocage framework

4. Conclusions

To sum up, a new POM-based 3D porous nanocage framework (H$_2$dap)[K(H$_2$O)$_2$ (V$_{10}$O$_{28}$)$_{0.5}$] (1) has been synthesized. In the structure of 1, two dap ligand molecules occupy in each POM-based inorganic nanocage. Furthermore, the electrochemical properties of 1 were studied, which indicate that 1 has good electrocatalytic activity towards reduction of iodate. Synthesis and property investigations on such POM-based 3D porous nanocage framework are in progress in our group.

Supplementary Information (SI)

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC number: 784651 or 1 (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, http://www.cam.ac.uk).

Acknowledgements

This work was financially supported by the NSF of China (No. 21603113), the NSF of Heilongjiang Province (No. QC2016014) and Undergraduate Training Programs for Innovation and Entrepreneurship of Qiqihar University (No. 201610221088).

References

11. Dolbecq A, Dumas E, Mayer C R and Mialane P 2010 Hybrid organic-inorganic polyoxometalate compounds:
from structural diversity to applications Chem. Rev. 110 6009
17. Kamata K, Nakagawa Y, Yamaguchi K and Mizuno N 2008 1,3-Dipolar cycloaddition of organic azides to alkynes by a dicopper-substituted silicotungstate J. Am. Chem. Soc. 130 15304
24. Brown I D and Altermatt D 1985 Bond-valence parameters obtained from a systematic analysis of the inorganic crystal structure database Acta Crystallogr. B 41 244